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Sampling of Reactive Atmospheric Species by Transition-Flow Reactor: Application to Nitrogen Species (Journal Version)

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16. ABSTRACT

Concentrations of nitric acid vapor and fine particulate nitrate were measured at the 1985 Nitrogen Species Methods Comparison Study at Claremont, California, with a transition-flow reactor, which separates the gases and particles by differential diffusion in a transition-flow stream and avoids sampling artifacts for these reactive species. Error analysis showed that [HNO_3] was determined with typical uncertainties 1σ of 5-8% and fine particulate [NO_3^-] at typical uncertainties of 5-11%. Both species showed a strong diurnal pattern with daytime maxima. Daytime [HNO_3] ranged from 25 to 495 nmole m^{-3}, while nighttime values ranged from less than 1 to 107 nmole m^{-3}. For 75% of tne time periods, HNO_3 and fine particulate NO_3^- concentrations were within a factor of two of each other. The time-weighted average concentrationns of 12 and 10 hour samples were equivalent to the corresponding 22 hour sample for each day. Simple filtration with Teflon and nylon filters in series overestimated [HNO_3] by 30-50% for 10 and 12 hour samples, and by 70% for 22 hour samples. Analysis of ionic balance suggests that the cause of the overestimate was dissociation of NH_4NO_3 from equilibrium changes, and not displacement by strong acids.

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THE SAMPLING OF REACTIVE ATMOSPHERIC SPECIES BY TRANSITION-FLOW REACTOR: APPLICATION TO NITROGEN SPECIES

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Abstract—Concentrations of nitric acid vapor and fine particulate nitrate were measured during the 1985 Nitrogen Species Methods Comparison Study at Claremont, California, with a transition-flow reactor. This system separates atmospheric gases and particles by differential diffusion in a transition-flow stream and thereby minimizes sampling artifacts for these reactive species. Error analysis showed that $[HNO_3]$ was determined with typical uncertainties (1σ) of 5–8% and fine particulate $[NO_3^-]$ at typical uncertainties of 5–11%. Both species showed a strong diurnal pattern with daytime maxima. Daytime $[HNO_3]$ ranged from 25 to 495 nmole m^{-3}, while night-time values ranged from less than 1 to 107 nmole m^{-3}. The time-weighted average concentrations of 12- and 10-h samples were equivalent to the corresponding 22-h sample for each day. Simple filtration with Teflon® and nylon filters in series over-estimated $[HNO_3]$ by 30–50% for 10- and 12-h samples, and by 70% for 22-h samples. Analysis of ionic balance suggests that the cause of the over-estimate was dissociation of NH_4NO_3 from equilibrium changes, and not displacement by strong acids.

Key word index: Nitric acid, nitrate, transition-flow reactor, nylon, acid rain.

INTRODUCTION

Nitric acid vapor (HNO_3) and fine particulate nitrate (NO_3^-) are important oxidation products of the NO_x emitted by mobile and stationary sources. Among the effects attributed to them are ecosystem acidification and materials damage (U.S. Environmental Protection Agency, 1982). Yet, because the partitioning of nitrate between gas and particle phases involves several important variables ($[HNO_3]$, $[NH_3]$, temperature, relative humidity and droplet pH), it is difficult to measure accurately their atmospheric concentrations. A common sampling approach has been to remove particles by filtration, then capture the gaseous HNO_3 by a selective adsorber; this is the filter pack method (Okita *et al.*, 1976). But even the use of an inert filter substrate such as polytetrafluoroethylene (PTFE) Teflon® for the particle filter may allow positive HNO_3 biases due to the dissociation of previously collected NH_4NO_3 particles or displacement of HNO_3 from NH_4NO_3 particles by strong acids, and negative HNO_3 biases due to premature removal onto accumulated non-inert particles as sampling progresses.

Our approach has been to employ a newly developed technique, the transition-flow reactor (TFR), in which HNO_3 is sampled from a transition-flow stream (Reynolds' number = 2600) by a selectively adsorbing liner (Durham *et al.*, 1986). In order to deposit, a species must cross a boundary layer of about 0.5 mm thickness and be adsorbed by a perfect sink wall. Only adsorbable species with sufficiently high diffusivities will deposit in sufficient quantities to be measured. Fine particles, whose diffusivities are considerably less than those of most gases, will be only slightly deposited. Thus there is good selectivity to measure gaseous HNO_3 in the presence of particulate NO_3^-. For our sampler's dimensions and flow rates, the fraction of HNO_3 collected is quite stable at about 0.09, allowing calculation of the mass of gaseous HNO_3 entering the sampler. Teflon® and nylon filters following the transition-flow section collect particulate NO_3^- and the remaining HNO_3; these NO_3^- values combined with the NO_3^- found on the nylon liner produce the total mass of NO_3^- entering the sampler. Particulate NO_3^- mass is then obtained as the difference between total NO_3^- and gaseous NO_3^- masses. Our sampler also measures NH_3 and particulate NH_4^+ (by transition-flow reactor), particulate SO_4^{2-} and gaseous SO_2 and NO_2 by using auxillary adsorbers (Knapp *et al.*, 1986).

EXPERIMENTAL

The sampler as operated at the September 1985 Nitrogen Species Methods Comparison Study in Claremont, California, is depicted in Fig. 1. Air is drawn through a cyclone to remove particles larger than about 2 μm aerodynamic diameter. At the cyclone's outlet, a vortex-removing tee disrupts the spin circulation imparted by the cyclone. The sample at a flow of 16.1 std. ℓ min^{-1} enters a tube containing 3.2 cm long liners of nylon (Membrana Nylasorb, M8PL, lot 2999) and Nafion® which remove about 9% of the gaseous nitric acid and about 17% of the ammonia, respectively, from the flow stream. The sample then passes through a PTFE Teflon® filter (Membrana Zefluor, P5PJ) to remove nitrate,

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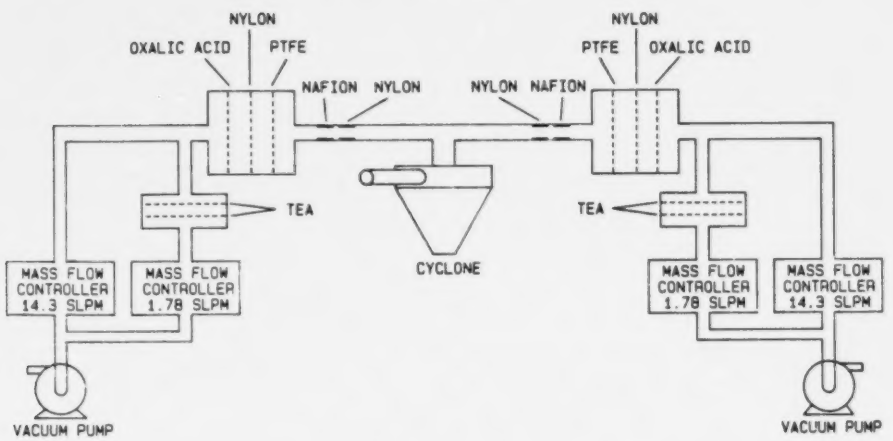

Fig. 1. The transition-flow reactor sampler as run at the September 1985 Nitrogen Species Methods Comparison Study at Claremont, California.

sulfate, and other particles, a nylon filter (Membrana Nylasorb, M9PL, lot 871) to collect the remaining HNO_3 and any HNO_3 released from NH_4NO_3 previously collected on the Teflon® filter, and an oxalic acid-coated filter to collect the remaining NH_3 and any NH_3 released from NH_4NO_3 previously collected on the Teflon® filter. The flow stream is then split: 1.78 std. ℓ min^{-1} goes through two triethanolamine-treated filters for collecting SO_2 and NO_2 and then to a mass flow controller and a pump. The second stream of 14.3 std. ℓ min^{-1} goes directly to another mass flow controller and the same pump. Except for the liners and filters, all surfaces contacting the sample stream are TFE Teflon®. The dual sampler was operated on a schedule in which one side operated for 22 h, while the other side operated for 12 h was replaced by a cleaned and reloaded section, and operated another 10 h.

Quality control and quality assurance activities (Ellestad, 1986) provided good confidence in our results. These activities included analysis of Air Resources Board-supplied Teflon® and nylon filters spiked with known amounts of NO_3^- and SO_4^{2-}, multiple analysis of most samples, sampling a HNO_3 source to verify our sampler's HNO_3 collection fraction, and on-site flow rate comparisons.

The uncertainty of measurements made with the sampler depends primarily on four sources of error: the fraction of HNO_3 or NH_3 removed by the liner, air sample volume, liner and filter blanks, and chemical analysis. The fraction of HNO_3 removed by the nylon liner was about 0.089 ± 0.002 (Durham *et al.*, 1986). Due to physical differences, the four sampling tubes used in the study actually had slightly lower or higher fractions, but for all tubes the estimated uncertainty was 0.002. For NH_3, the fraction removed by the Nafion® liner was about 0.17 ± 0.017.

The mass flow controllers were calibrated to standard conditions (0°C, 760 torr) with a certified dry test meter on-site before, during, and after the study. Only very slight changes (< 2%) were found. The estimated uncertainty in the sample volumes is 3%.

Five sets of blank liners and filters were obtained during the study by unloading routinely prepared but unused samplers. Blank levels were uniform and low compared to most of the loadings (Table 1). The standard deviations of blanks were included in estimating uncertainties of net loadings.

Nitrate masses on the nylon and Teflon® media were analyzed on a Dionex model 14 ion chromatograph having a detection limit of 0.005 μg ml^{-1}. Standard laboratory practices were augmented for this study by extra comparisons

Table 1. Mean blank values in μg ($n = 5$)

	Mean	1σ
Nylon liner, NO_3^-	0.32	0.02
Nafion® liner, NH_3	1.71	0.06
Teflon® filter, NO_3^-	0.57	0.32
Teflon® filter, NH_4^+	1.77	0.45
Nylon filter, NO_3^-	~0.05	~0.01
Oxalic acid filter, NH_4^+	2.1	0.9
TEA filter pair, NO_2^-	1.0	0.3
TEA filter pair, NO_3^-	0.6	0.2

Table 2. Nitrate analysis results (μg) for three ARB-supplied filters at each loading

Known	Analyses for three filters
9.9 on nylon	10.3, 10.3, 10.5
69 on nylon	70.4, 70.1, 70.5
198 on nylon	200, 199, 199
24.9 on Teflon®	25.0, 25.1, 25.0
74.9 on Teflon®	75.6, 76.1, 75.5
249 on Teflon®	250, 251, 250

with external reference standards, duplicate analyses of all samples, and calibration of the ion chromatograph several times each day. The accuracy of our nitrate standards compared to the ARB-supplied nylon and Teflon® filters was very good (Table 2). The estimated uncertainty due to accuracy and precision is 4% (or 0.05 μg, if larger).

Nafion® liners were analyzed with an Orion model 95–12 specific ion electrode having a detection limit of 0.05 μg ml^{-1}. Standards were prepared from an Orion-certified stock solution and compared to in-house and EPA-EMSL reference standards. We estimate the accuracy of the NH_3 analysis at 10%. Seven of the 24 Nafion® samples were re-analyzed; on the average, results agreed to within 2%. The resulting uncertainty due to accuracy and precision is therefore estimated at 10%.

NH_4^+ analyses of the Teflon® and oxalic acid filters were performed by a contractor using a Technicon Auto-Analyzer

having a detection limit of 0.05 $\mu g\,ml^{-1}$. The contractor's standards were verified using blind samples spiked with an in-house reference standard, producing an estimated analytical accuracy of 4%. Ten of the 48 samples were re-analyzed; on the average, results agreed to within 3%. The resulting uncertainty due to accuracy and precision is therefore estimated at 5%.

Triethanolamine (TEA) treated filters were analyzed for NO_2^- and NO_3^- by ion chromatography with both filters from one run extracted together. While most of the NO_2 collected by the TEA filters was analyzed as NO_2^-, a portion (typically 23% for day samples and 6% for night samples) occurred as NO_3^-.

Because of apparent interaction of TEA with the AS-3 analytical column, NO_2^- results were low by 0–5% and NO_3^- results were low by 4–20%, depending on concentration, as determined by analyzing TEA filters spiked with known amounts of the ions. Three levels of spiking and three filters at each level were used. The precision of the correction factor was determined by multiple analyses of the spiked filters. In addition, the TEA-column interaction degraded the precision of the sample analyses and produced detection limits of about 0.05 $\mu g\,ml^{-1}$ for both ions. For NO_2^-, we estimate the uncertainty at 6%, and for NO_3^- at 10%.

Uncertainties estimated above were propagated using standard techniques: the uncertainty of a calculated quantity was estimated as the square root of the sum of the squares of the uncertainties of each measured variable, with each term weighted by the partial derivative of the function with respect to that variable. Uncertainties were calculated for each net mass loading, based on the accuracy and precision of the technique at the measured concentration and on the blank variance. These uncertainties were combined with the 3% uncertainty in volume measurements and, where applicable, the 2% or 10% uncertainty in the trace gas removal fraction. The resulting overall uncertainties (1σ) were: HNO_3: 5–8%; fine NO_3^-: 5–11%; NH_3: 15–20%; fine NH_4^+: 12–36%; and NO_2: 6–7% (5th and 95th percentile values shown).

RESULTS AND DISCUSSION

Both $[HNO_3]$ and fine particulate $[NO_3^-]$ showed a strong diurnal pattern with daytime maxima (Fig. 2). There was clearly a photochemical episode from 12 to 17 September with a maximum on 14 September. Daytime $[HNO_3]$ ranged from 25 to 495 nmole m^{-3}, while night-time values ranged from less than 1 to 107 nmole m^{-3}. For 75% of all time periods shown, $[HNO_3]$ and fine particulate $[NO_3^-]$ were within a factor of two of each other. The time-weighted averages of day–night results were compared to the results of the sampler that operated over the same 22-h periods. The comparison for total nitrate is excellent; the mean difference is only 3% (Fig. 3). For HNO_3, the mean ratio of day–night/22 h is 1.12 ± 0.11, indicating no statistically significant bias due to sampling duration. $[NH_3]$ showed several episodes, but there was no consistent diurnal cycle for $[NH_3]$ or $[NH_4^+]$ (Fig. 4). For NH_3, the mean ratio of day–night/22 h is 1.05 ± 0.11. $[NO_2]$ showed a diurnal cycle with night-

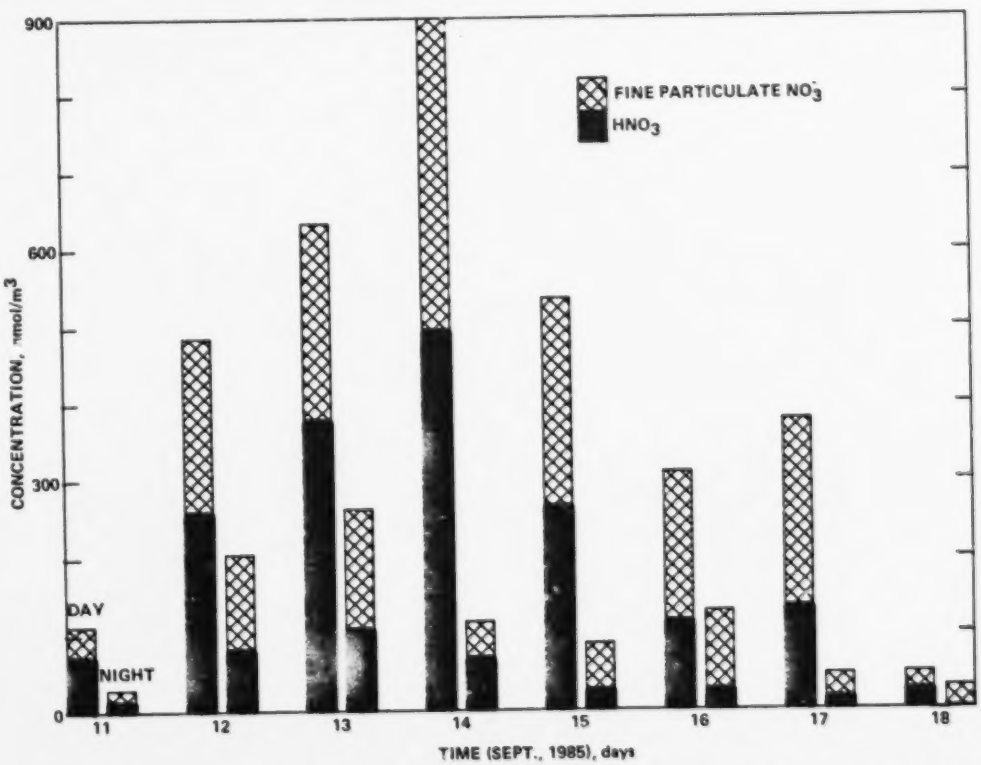

Fig. 2. Nitric acid and fine particulate nitrate concentrations during the study as measured by the transition-flow reactor. The left bar of each pair is daytime (0800–1950); the right is night-time (2000–0600).

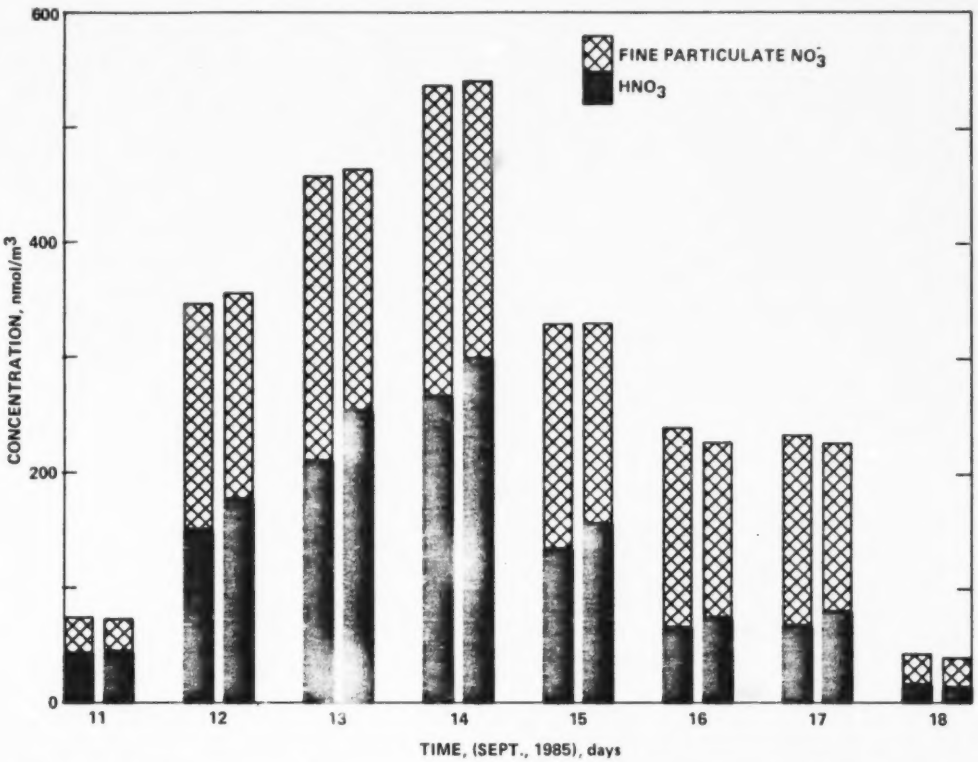

Fig. 3. Comparison of nitric acid and fine particulate nitrate concentrations measured by the transition-flow reactor for 22-h samples (left bar of each pair) vs the time-weighted average of corresponding 12- and 10-h samples (right bar of each pair).

time concentrations usually 50–100% higher than daytime concentrations (Fig. 5). Its mean ratio of day–night/22 h shows good consistency: 0.96 ± 0.07.

A conventional filter pack (i.e. a Telfon® filter followed by a nylon filter) will over-estimate $[HNO_3]$ if NH_4NO_3 particles on the Teflon® filter dissociate or undergo reactions with strong acid particles, releasing HNO_3 which is then trapped by the nylon filter. Data from the TFR can be interpreted as a conventional filter pack by combining the nitrate found on the nylon liner with that on the nylon filter, where it presumably would have been retained had the nylon liner not been present. Daytime data show an average 55% over-estimate of $[HNO_3]$ by the filter pack (Table 3). Night-time data show over-estimates of about 30% by the filter pack and the 22-h data show over-estimates of about 70%. We suspect that the longer the sampling interval, the more opportunity for change in the equilibrium conditions affecting partitioning of HNO_3, NH_3 and NH_4NO_3, and thus more chance for positive bias of the filter pack for $[HNO_3]$. These data show that simple filter packs may produce significant errors in the measurement of HNO_3 vapor. It may be untenable to apply a correction for the over-estimate because the cause(s) may or may not be present at different times at different places and may occur in varying magnitudes.

Table 3. Ratios of filter-pack interpretation of data to true $[HNO_3]$ measured by the transition-flow reactor. 95% confidence limits are shown

Sept. 1985	Day	Night	22-h
11	1.46 ± 0.22	0.99 ± 0.20	1.47 ± 0.23
12	1.45 ± 0.22	1.43 ± 0.25	1.70 ± 0.25
13	1.54 ± 0.24	1.43 ± 0.22	1.79 ± 0.26
14	1.50 ± 0.23	1.25 ± 0.20	1.65 ± 0.24
15	1.68 ± 0.24	1.27 ± 0.27	1.94 ± 0.28
16	1.65 ± 0.24	1.19 ± 0.25	1.75 ± 0.27
17	1.54 ± 0.22	1.40 ± 0.26	1.85 ± 0.28
18	1.56 ± 0.26	*	1.63 ± 0.29
Means	1.55 ± 0.23	1.28 ± 0.24	1.72 ± 0.26

* Not included in statistics because of abnormally high ratio.

To estimate non-NH_4^+ cation concentrations (a substantial portion of which is undoubtably H^+), we performed an ionic balance using our sampler's SO_4^{2-}, NO_3^- and NH_4^+ data:

$$\langle [\text{non-}NH_4^+ \text{ cations}] \rangle = 2[SO_4^{2-}] + [NO_3^-] - [NH_4^+]. \quad (1)$$

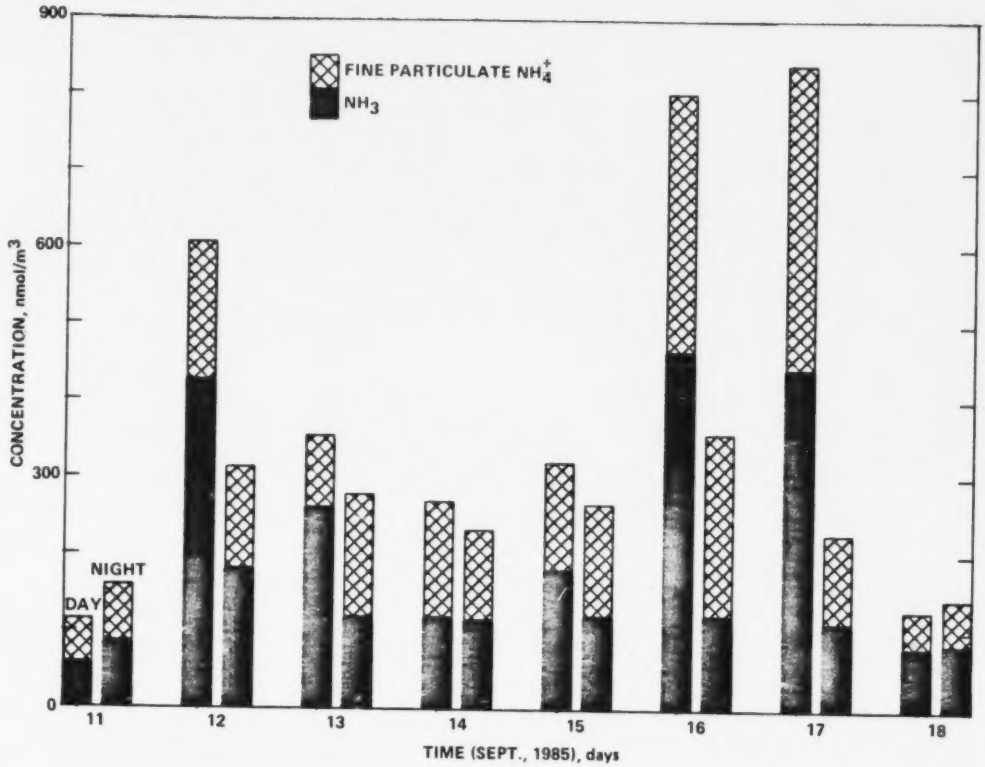

Fig. 4. Ammonia and fine particulate ammonium concentrations during the study as measured by the transition-flow reactor.

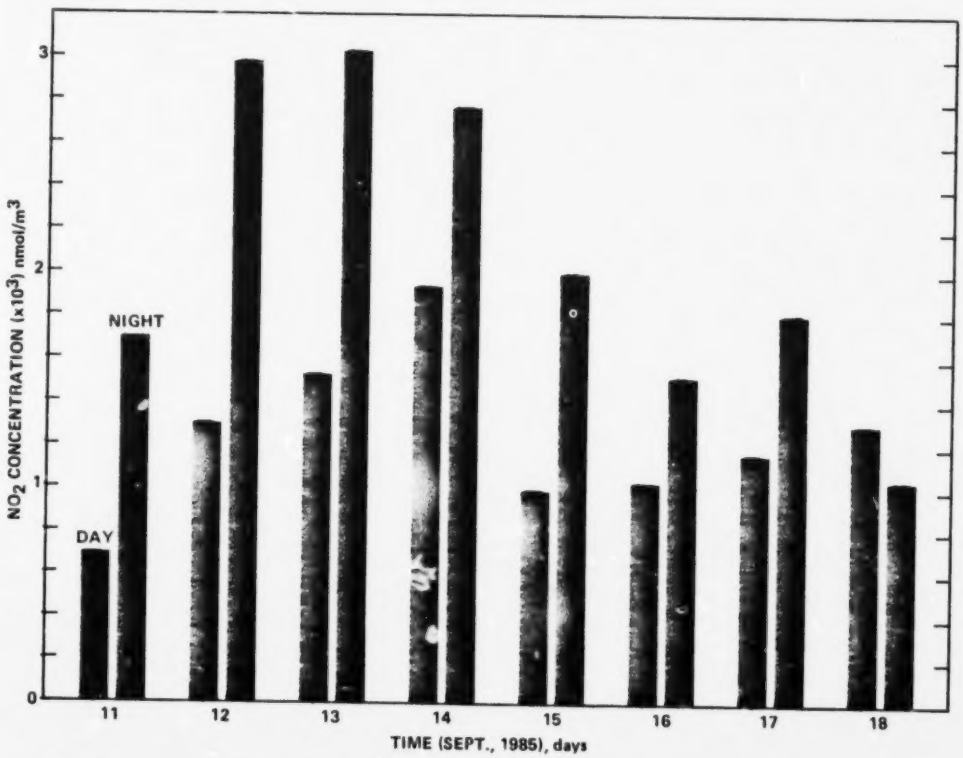

Fig. 5. Nitrogen dioxide concentrations during the study as measured by triethanolamine-treated filters.

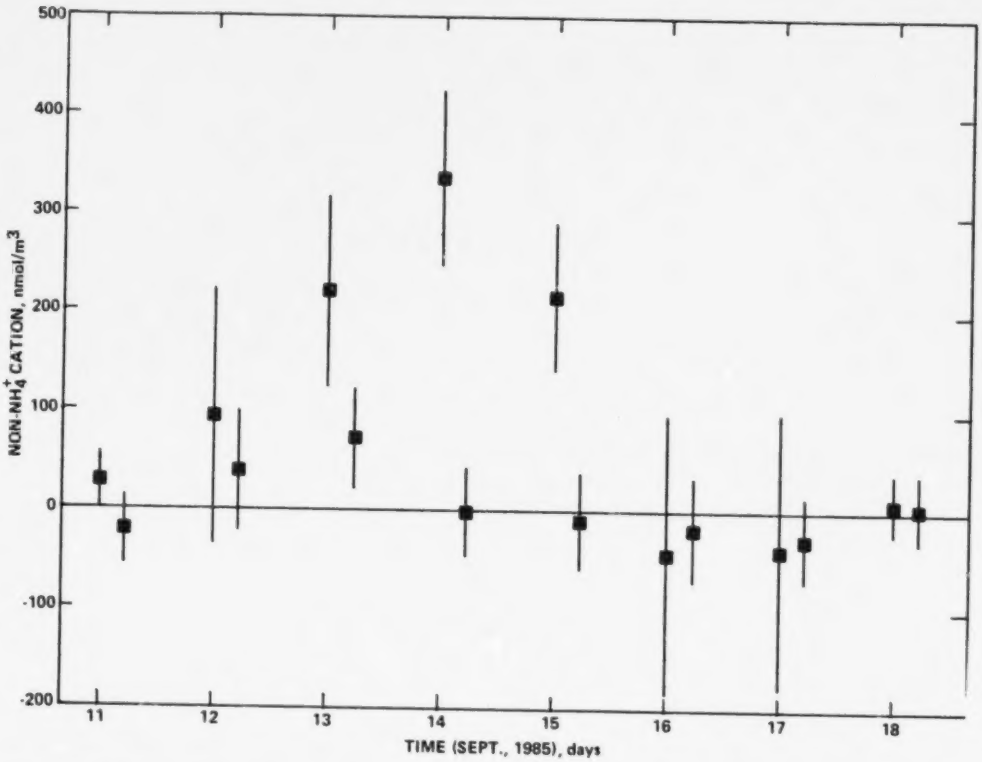

Fig. 6. Estimated non-NH_4^+ cation concentrations during the study. Ninety-five per cent confidence limits are shown.

The results are shown in Fig. 6. Data whose confidence limits do not include zero may reasonably be considered to have significant concentrations of non-NH_4^+ cations. The significant points agree with the HNO_3 data on the existence of an episode centered on 14 September.

Consideration of Table 3 and Fig. 6 suggests that during this study the displacement of HNO_3 from NH_4NO_3 particles during sampling was not the dominant mechanism causing the filter pack to overestimate $[HNO_3]$. Statistically significant overestimates of $[HNO_3]$ by filter pack occurred for every day and about half the night periods. Yet only four daytime periods showed significant concentrations of non-NH_4^+ cation. A linear regression of the overestimate ratio to [non-NH_4^+ cation] for these four periods had $r = 0.29$. A similar analysis of 22-h data also had four periods with statistically significant [non-NH_4^+ cation]; for this data the regression had $r = -0.53$, indicating that another mechanism, presumably dissociation due to equilibrium change, was at work.

CONCLUSIONS

The transition-flow reactor sampler was successfully operated to sample HNO_3 and fine particulate NO_3^- with (1σ) uncertainties of about 5–10% at the 1985 Nitrogen Species Methods Comparison Study. Analysis of its data demonstrates that simple filter pack samplers (a Teflon® filter followed by a nylon filter) may significantly over-estimate $[HNO_3]$, and that the over-estimate may increase with longer sampling durations. From other nitrogen and sulfur data measured by the transition-flow reactor sampler in an ionic balance analysis, it is inferred that dissociation of NH_4NO_3 due to changed equilibrium, and not displacement by strong acids, is the cause of the overestimates of $[HNO_3]$ by filter packs.

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